Ecocomposites Reinforced with Cellulose Nanoparticles:
An Alternative to Existing Petroleum Based Polymer Composites

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Drivers for This Program

1. **Sustainability**
   Use renewables safely and responsibly

2. **Nanotechnology**
   surface, surface, surface

3. **Policy /Regulation**
   • Biomass R&D Act of 2000
   • Farm Bill 2002, Title IX

**Willow Project**

**Biorefinery**

**Products**
Bioplastic, Biofuels, Nanoparticles for reinforced bioplastics
4.19. ... society needs to develop effective ways of dealing with the problem of disposing of mounting levels of waste products and materials. Governments, together with industry, households and the public, should make a concerted effort to reduce the generation of wastes and waste products by:

(a) Encouraging recycling in industrial processes and at the consumer level;
(b) Reducing wasteful packaging of products;
(c) Encouraging the introduction of more environmentally sound products.
Why Biodegradable?

- Sustainable
- Regulations

on disposal

Classical
Plankton, Bacteria

10^6 yrs
heat
pressure

Crude Oil
Process

Monomers

Polymer Rich Organism
Process

Polymer

1990

Ferment, heat, stir nutrients
2-5 days

2003

Genetically Modified Plants

sunlight, air, rain nutrients growing season
Nanoparticles

• At least 1 dimension < 100 nm (10^{-7} m) - NSF

• 2 Advantages of Nanotechnology
  – **Speed** of light: \(3 \times 10^{10} \text{ cm/sec} \times 10^{-9} \text{ s/ns}\)
    \[1 \text{ ns} = 30 \text{ cm} \text{ (1 foot)} \text{ mostly useful in electrical applications}\]
  – Increased **specific surface area**
    • Influences catalysis, adhesion
Nanocomposites

- Particulate composites:
  - Matrix
  - Particulate Phase

- Reinforcing particles have at least one dimension (i.e. length, width, or thickness) on the nanometer scale

Why small?

Surface area: $5 \times 5 \times 6 = 150$

$125 \times (1 \times 1 \times 6) = 750 = 5 \times 150$

In proceeding from a $\mu$m to nm scale the specific surface area increases by 3 orders of magnitude
**Surface Area vs. Aspect Ratio**

**Montmorillonite Clay:**
- Length: 1 nm
- Diameter: 200 – 400 nm
- Aspect Ratio: 0.005 – 0.0025 (200 – 400)

**Cellulose Nanocrystals:**
- Length: 100 – several µm
- Diameter: 3 – 20 nm
- Aspect Ratio: 10 – 10,000
Cellulose Morphology

Fiber (cell)

White pine tracheids – Helm, Va Tech

Wood Cell Schematic

Microfibril
Hanna, ESF
Parenchyma Cells

- Predominant cell type in fruit
- Primary cell wall tissue
- Rays in woody tissue
Microfibril size

Algae                                 Tunicate

Valonia 20 nm

Cotton        Wood        Sugar Beet
Biomass from Fruit and Sugar Processing

4.3 Mt/yr USDA 2002
40% > juice

Sugar Beets
27 Mt/yr USDA 2002
1 ton beets > 110 lb pellets

12.4 Mt/yr USDA 2002
Composition of Orange Byproduct

Weight %

- Cellulose: 26.6%
- Lignin: 7%
- Fiber: 22.1%
- Water: 14.9%
- Protein: 9.9%
- Fat: 19.4%

Total: 100%
Composition of Apple
Pomace
Weight %

- Cellulose: 27.3%
- Lignin: 4.7%
- Fiber: 7.4%
- Water: 11.5%
- Protein: 21.6%
- Fat: 21.1%

Chiellini (2001) *Biomacromol* 2:1029-1037
Sugar Beet Pulp Cellulose

• 20% cellulose, 25-30% hemicellulose and 25-35% pectin, sucrose, proteins, lignin, fat
• Individual microfibrils 2 - 4 nm in diameter
### Nanoparticle Samples

#### Sources Utilized
- Apple Pomace
- Bagasse
- Chitin
- Orange Pulp
- Sugar beet
- Tunicate
- Wheat
- Wood

#### Derivatives Made
- Acetates
- Maleates
- N-Acetyl (chitin)
- Trimethylsilyl

#### Derivatives Planned
- Amino
- Carboxylate
- Fatty acid
Crystal and Microfibril Preparation

Extraction, Bleaching:

1. Dewax- Soxhlet
2. Mill
3. Alkali solution
4. Sodium chlorite
5. homogenize

Hydrolysis (for nanocrystals):

- acid (HCl, H₂SO₄)
- concentrations (65%)
- temperature (40°C)
- hydrolysis time (1 – 2 h)
- acid-to-substrate ratio (0.1)
Bacterial Cellulose

- *Acetobacter xylinum*
- Ribbons: rectangular cross-section of 50 x 0.8 nm
Apple Pomace /Cellulose XRD

Cellulose I
Size from Line broadening
\( \sim 3 \text{ nm} \)

As received:
After bleaching, dispersion and re-drying
Are Parenchymal Celluloses Unusual??

After 9% NaOH

The sudden and essentially complete disappearance of microfibril structure is dramatically different from the gradual loss of microfibril size found in secondary wall mercerization.

After 10% NaOH

After 12% NaOH

n and \( d_2 \) are variables and act as a \( T_2 \) filter which allows the selective removal of signals associated with short \( T_2 \) values (rigid components, crystal interior).
HR vs CP MAS NMR

HRMAS CPMG active  
CPMAS active
Parenchyma Fibers Have Pectin Rich Surfaces

Raw apple pomace  Purified Cellulose

\[ n=10, \quad d2=1500 \, \mu s \]

\[ \text{No evidence of methylation in CP/MAS} \]

\[ \text{Methyl groups (pectin) reside on the mobile surface seen by HR/MAS, not in the interior.} \]
Possible interactions at the filler matrix interface

D43T4 Eastar Bio

Maleated Cellulose MF
Dynamic Mechanical Analysis

Different Reinforcing Mechanisms ?????

Eastar Bio
Eastar + '10%MF
Eastar + 30%MF
Series6
Eastar + 10%NC
Eastar + 20%NC
Eastar + 30%NC
Scale Up

June 2004: Purchased a 22 l reactor to make nanoparticles in larger quantities

July 2004: First run 65% H$_2$SO$_4$ @ 40° C for 2h

400 gm wood pulp
Final yield = 280 g (70% conversion)

Problems / Challenges

Separation of particles from acid
Acid recycling?
Minimizing reaggregation
TEBOL(t-BuOH) ppt
What’s Ahead

1. Reactive Extrusion - Can we improve the association by covalent links from particles matrix molecules?

2. Biodegradability Plastic (GreenPla®???)
   - Currently review ASTM and other standards.
Conclusions

1. Cellulose Nanoparticles can be made from almost any kind of biomass,
2. The properties of the particles may vary with source due to species dependent differences in mean particle size,
3. Scale up of our preps, now in progress, will permit more widespread testing,
4. New techniques are needed to characterize surface chemistry and interactions,
5. Reactive extrusion may provide a route to stronger composites. (speculation at this point),
6. An acid free or reduced process may come from treating the nanoparticles as a coproduct of ethanol production from biomass.
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